Five-photon absorption and selective enhancement of multiphoton absorption processes

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Abstract

We study one-, two-, three-, four- and five-photon absorption of three centrosymmetric molecules using density functional theory. These calculations are the first *ab initio* calculations of five-photon absorption. Even- and odd-order absorption processes show different trends in the absorption cross sections. The behaviour of all even-

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and odd-photon absorption properties shows a semi-quantitative similarity which can be explained using few-state models. This analysis shows that odd-photon absorption processes are largely determined by the one-photon absorption strength whereas all even-photon absorption strengths are largely dominated by the two-photon absorption strength, in both cases modulated by powers of the polarizability of the final excited state. We demonstrate how to selectively enhance a specific multiphoton absorption process.

The concept of multiphoton absorption (MPA) dates back to 1931 when it was predicted theoretically by Maria Göppert-Mayer.[1] After the introduction of high-intensity laser light sources, multiphoton absorption has gained a lot of attention during the past five decades, with the first experimental proof for two-photon absorption as the starting point in 1961.[2]

Two-photon absorption has by now found a wide range of applications.[3–6] Simultaneously, electronic excitations involving absorption of up to five photons has been observed experimentally.[7] The theoretical treatment of multiphoton absorption has also been pushed forward during the last decades, and computational methods for the calculation of two-photon transition strengths are available for SCF-based[8,9] as well as for correlated wave-function based methods.[10–13] Implementations of three-photon absorption have been realized only for SCF-based methods[14–16] but SCF-based density-functional theory studies give good agreement with experiment for TPA and 3PA processes for small and medium-sized molecules.[17,18] In our group, a recursive open-ended response theory[19] has been expanded to the treatment of single residues of response functions, enabling the calculation of multiphoton absorption cross sections to infinite order using SCF-based methods, with results having been reported for four-photon absorption.[20]

In order to design molecules with high multiphoton absorption cross sections, general and qualitative structure-property relations are important. However, very few general structure-property relations exist for higher-order multiphoton absorption properties, al-

though some interesting observations have been made in the case of three-photon absorption.[21,22] The major scope of this work is both to present the first computational treatment of five-photon absorption and to study the relations between different multiphoton absorption processes. As experimental data for four- and five-photon absorption are very limited, in particular when it comes to complete spectra, we have to rely on a computational treatment of these properties to compare their behaviour. In order to amplify the general observations presented here, we will focus on centrosymmetric molecules.

The multiphoton absorption cross sections calculated for the molecules in Fig. 1 are shown in Table 1 for the *p*-dinitrobenzene (PDNB) molecule, which has D_{2h} symmetry, and in Fig. 2 for the diaminoazobenzene (C_i symmetry) and indigo molecules (C_{2h} symmetry). Note that the units for the absorption cross sections differ and that the cross sections differ by orders of magnitude. The results reported have been calculated using the CAM-B3LYP functional[23] and the augmented correlation-consistent polarized valence double-zeta basis sets (aug-cc-pVDZ) of Dunning and Woon.[24,25] A recent study has shown that this level of theory is a good compromise between accuracy and computational cost.[20] The calculations have been performed using a recursive response theory code[19,20] interfaced to a development version of the Dalton program.[26]

There are remarkable parallelities in the absorption behaviour of the different states depending on whether an even or an odd number of photons is absorbed, see Table 1. The PDNB molecule deviates from this observation with its A_u states which cannot be reached by one-photon processes for symmetry reasons.

Table 1: Calculated MPA cross sections for PDNB and their ratios.

No.	Energy [eV]		irrep	jPA cross sections [$\mathrm{cm}^{2j}\mathrm{s}^{j-1}/\mathrm{photon}^{j-1}$]					Cross section ratios			
				OPA (10^{-19})	TPA (10^{-54})	3PA (10^{-86})	4PA (10^{-118})	5PA (10^{-150})	OPA/3PA (10^{62})	TPA/4PA (10^{61})	3PA/5PA (10^{62})	OPA/5PA (10^{128})
1	3.90	1	b3g		3.44		0.08			43860		
2	3.95	1	au			0.04		0.02			269	
3	4.39	1	b2g		9.26		0.96			9689		
4	4.42	1	b1u	2.46		1.78		0.13	138013		1338	18466
5	4.62	1	b2u	89.4		803		65.5	11132		1226	1365
6	5.03	1	b3u	1240		52557		13226	2359		397	94
7	6.06	2	b2u	278		1695		1911	16390		89	145
8	6.06	1	b1g		29100		263357			110		
9	6.15	1	ag		801169		3041400			263		
10	6.20	2	b1g		21602		4893130			4		
11	6.68	2	b2u	607		7395		42997	8220		17	14
12	6.79	2	b3u	1626		60375		412524	2693		15	4
13	6.82	2	au			2.93		1.27			231	
14	6.85	2	b3g		1.90		2.57			740		
15	6.92	3	au			25.1		1.48			1694	

Investigating the results, we note that the qualitative agreement between the absorption cross sections is not as obvious for the even-order processes as for odd-photon absorption processes. The best correlation between the different even-photon absorption processes has been found in the diaminoazobenzene molecule.

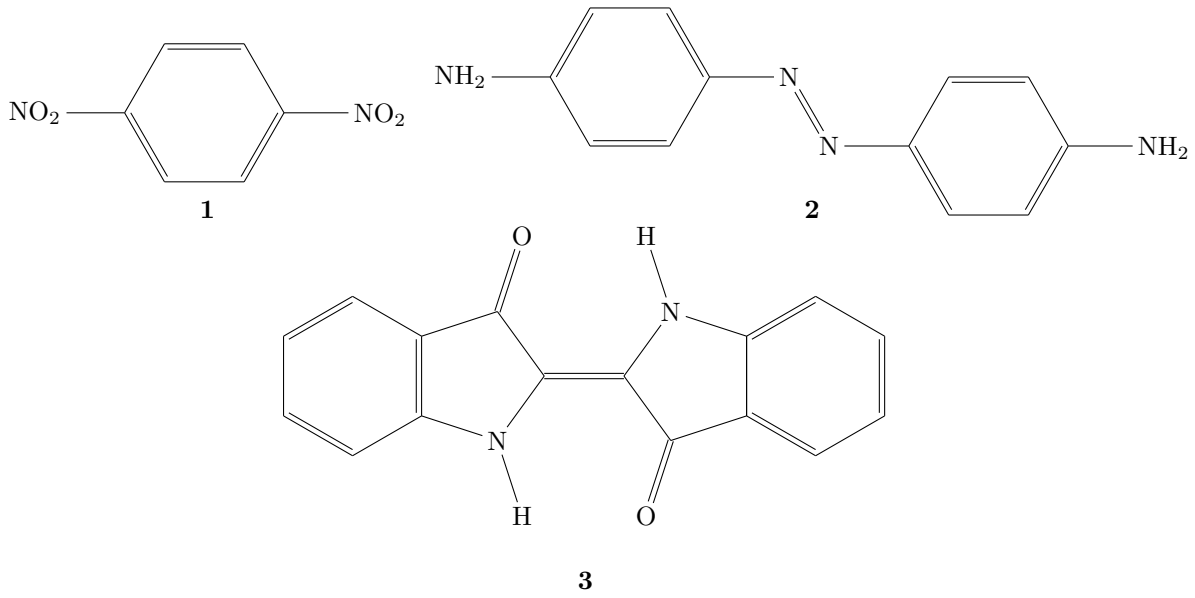
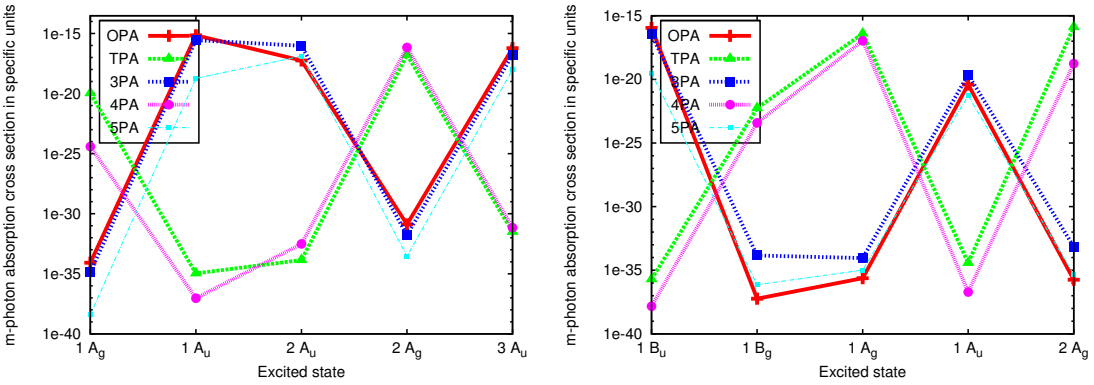


Figure 1: The three centrosymmetric molecules that have been studied in this work: *para*-dinitrobenzene (**1**), diaminoazobenzene (**2**) and indigo (**3**).

The similarity in the multiphoton absorption cross sections observed in Fig. 2 can be explained by considering the sum-over-states expression for the multiphoton absorption cross sections. For a complete discussion of the basic theory of multiphoton absorption we refer to the literature[20,27–30] and we restrict ourselves here only to provide the general expression for the multiphoton absorption cross sections that we will use in the analysis and to show an appropriation we do in order to explain our observations.



(a) Diaminoazobenzene (b) Indigo

Figure 2: Multiphoton absorption behaviour of the three molecules under investigation. TPA cross sections have been scaled with 10^{32}. 3PA cross sections are scaled with 10^{65}, 4PA cross sections are scaled with 10^{94} and 5PA cross sections are scaled with 10^{126}.

The general j-photon absorption cross section $\sigma^{j\mathrm{PA}}$ is proportional to the square of the j-photon transition matrix element $\mathbf{M}^{j\mathrm{PA}}$ for $j \geq 2$[20,27]

$$\sigma^{j\mathrm{PA}} \sim |\mathbf{M}^{j\mathrm{PA}}|^2, \tag{1}$$

with $\mathbf{M}^{j\mathrm{PA}}$ being defined as (atomic units)[29]

$$\mathbf{M}^{j\mathrm{PA}} = \mathcal{P}^{X_1,X_2,\ldots,X_j} \sum_{l_1,l_2,\ldots,l_{j-1}} \frac{\langle 0|\mu_{X_1}|l_1\rangle\langle l_1|\mu_{X_2}|l_2\rangle\ldots\langle l_{j-1}|\mu_{X_j}|f\rangle}{(\omega_1-\omega_{l_1})(\omega_1+\omega_2-\omega_{l_2})\ldots(\omega_1+\omega_2+\ldots+\omega_{j-1}-\omega_{l_{j-1}})}, \tag{2}$$

where ω_i is the frequency of perturbation X_i and where we have already used the fact that the ground-state dipole moment vanishes for centrosymmetric molecules.[30] μ_{X_i} is the dipole operator with respect to perturbation X_i and ω_{l_i} is the excitation energy between the ground state 0 and the excited state l_i. f is the final state of the excitation and the operator $\mathcal{P}^{X_1,X_2,\ldots,X_j}$ generates all permutations of the perturbations. j is the number of photons absorbed in the described process. The calculations we present in this article have

been performed using this equation. To interprete them we now simplify this expression using symmetry considerations.

For centrosymmetric molecules we can easily identify the symmetry of the accessible final states f as well as the intermediate states l_i in Eq. (2). Because all electric dipole perturbations are *ungerade* and the ground state always *gerade*, the excited state l_1 that appears in the numerator of Eq. (2) must be *ungerade*. All final states for odd-photon absorption processes must be *ungerade*. In contrast, TPA and all higher-order even-photon absorption processes are only allowed for excitations with *gerade* final states.

However, from Fig. 2 and Table 1, we note that there is even a semi-quantitative agreement between the absorption cross sections of different excited states. The orders of magnitude that are covered by the different cross section values are very similiar in all cases, and the order of the states with respect to their MPA behaviour is similar within the even- and odd-photon absorption groups. This is illustrated in particular by the ratios between the cross sections that have been calculated for the PDNB molecule. Apart from the one for the $1B_{1u}$ state, which shows a rather small cross section, we find that all ratios between OPA and 3PA are within the range of about an order of magnitude. The behaviour of the TPA/4PA-ratios is rather similar with the exception of the one for the $1B_{1g}$-state. We will return this anomaly.

In order to explain these observations, we first give the explicit expressions for the one- and two-photon absorption matrix elements

$$M_a^{\mathrm{OPA}} = \langle 0|\mu_a|\mathcal{U}_f\rangle, \tag{3}$$

$$M_{ab}^{\mathrm{TPA}} = \mathcal{P}^{ab} \sum_{k=1}^{n_{\mathcal{U}}} \frac{\langle 0|\mu_a|\mathcal{U}_k\rangle\langle \mathcal{U}_k|\mu_b|\mathcal{G}_f\rangle}{\omega_a - \omega_{\mathcal{U}_k}}, \tag{4}$$

where the individual perturbations are marked by lowercase letters. $\mathcal{U}$ and $\mathcal{G}$ represent *ungerade* and *gerade* states, respectively, and the index f marks the final state. $n_{\mathcal{U}}$ is the

number of *ungerade* excited states that are symmetry allowed. The operator $\mathcal{P}$ generates all permutations of the perturbations and their individual frequencies.

Let us now consider the 3PA transition matrix element

$$M_{abc}^{\mathrm{3PA}} = \mathcal{P}^{abc} \sum_{k=1}^{n_{\mathcal{U}}} \sum_{l=1}^{n_{\mathcal{G}}} \frac{\langle 0|\mu_a|\mathcal{U}_k\rangle\langle \mathcal{U}_k|\mu_b|\mathcal{G}_l\rangle\langle \mathcal{G}_l|\mu_c|\mathcal{U}_f\rangle}{(\omega_a - \omega_{\mathcal{U}_k})(\omega_a + \omega_b - \omega_{\mathcal{G}_l})}. \tag{5}$$

For a molecule with a strong, isolated OPA state, the dominating excited state of *ungerade* symmetry is the final state of interest, in the spirit of few-state models for multiphoton absorption cross sections, the 3PA matrix element reduces to

$$M_{abc}^{\mathrm{3PA}} \approx \mathcal{P}^{abc} \sum_{l=1}^{n_{\mathcal{G}}} \frac{\langle 0|\mu_a|\mathcal{U}_f\rangle\langle \mathcal{U}_f|\mu_b|\mathcal{G}_l\rangle\langle \mathcal{G}_l|\mu_c|\mathcal{U}_f\rangle}{(\omega_a - \omega_{\mathcal{U}_f})(\omega_a + \omega_b - \omega_{\mathcal{G}})}. \tag{6}$$

Note that in this expression the summation over the *ungerade* states has been dropped but the summation over *gerade* states is not affected. The validity of this approach has been shown e.g. in work by Vivas and coworkers where a three-level model for TPA yielded impressing results compared to experiment.[31] Using this expression, we can write the 3PA matrix element as

$$M_{abc}^{\mathrm{3PA}} \approx \mathcal{P}^{abc} \frac{M_a^{\mathrm{OPA}}}{(\omega_a - \omega_{\mathcal{U}_f})} \cdot \sum_{l=1}^{n_{\mathcal{G}}} \frac{\langle \mathcal{U}_f|\mu_b|\mathcal{G}_l\rangle\langle \mathcal{G}_l|\mu_c|\mathcal{U}_f\rangle}{(\omega_a + \omega_b - \omega_{\mathcal{G}})}. \tag{7}$$

This quasi-few-state model now explains the similarity of the OPA and 3PA absorption cross sections, the 3PA cross section being proportional to the OPA cross section, the proportionality factor being the excited-state polarizability divided by an energy denominator. The permutation operator which is still present in the approximated equation takes into account that several spatial components of M_a^{OPA} can contribute to the transition dipole moment.

This is also an explanation for the low 3PA and 5PA cross sections of the A_u states in

PDNB since these states cannot be dominated by an OPA excitation according to Eq. (6). We can therefore separate 3PA excitations into *OPA-dominated* and *pure*-3PA absorptions.

We can extend this analysis to 4PA. The matrix element for four-photon absorption is

$$M^{\mathrm{4PA}}_{abcd} = \mathcal{P}^{abcd} \sum_{k=1}^{n_{\mathcal{U}}} \sum_{l=1}^{n_{\mathcal{G}}} \sum_{m=1}^{n_{\mathcal{U}}} \frac{\langle 0|\mu_a|\mathcal{U}_k\rangle\langle\mathcal{U}_k|\mu_b|\mathcal{G}_l\rangle\langle\mathcal{G}_l|\mu_c|\mathcal{U}_m\rangle\langle\mathcal{U}_m|\mu_d|\mathcal{G}_f\rangle}{(\omega_a - \omega_{\mathcal{U}_k})(\omega_a + \omega_b - \omega_{\mathcal{G}_l})(\omega_a + \omega_b + \omega_c - \omega_{\mathcal{U}_m})}, \tag{8}$$

where both the summations over k and m cover the same manifold of *ungerade* states. In the same manner, we can now assume a dominant contribution from $\mathcal{G}_f$ as the intermediate *gerade* state, and write Eq. (8) as

$$M^{\mathrm{4PA}}_{abcd} \approx \mathcal{P}^{abcd} \sum_{k=1}^{n_{\mathcal{U}}} \sum_{m=1}^{n_{\mathcal{U}}} \frac{\langle 0|\mu_a|\mathcal{U}_k\rangle\langle\mathcal{U}_k|\mu_b|\mathcal{G}_f\rangle\langle\mathcal{G}_f|\mu_c|\mathcal{U}_m\rangle\langle\mathcal{U}_m|\mu_d|\mathcal{G}_f\rangle}{(\omega_a - \omega_{\mathcal{U}_k})(\omega_a + \omega_b - \omega_{\mathcal{G}_f})(\omega_a + \omega_b + \omega_c - \omega_{\mathcal{U}_m})} \tag{9}$$

$$\approx \mathcal{P}^{abcd} \left(\frac{M^{\mathrm{TPA}}_{ab}}{(\omega_a + \omega_b - \omega_{\mathcal{G}_f})} \cdot \sum_{m=1}^{n_{\mathcal{U}}} \frac{\langle\mathcal{G}_f|\mu_c|\mathcal{U}_m\rangle\langle\mathcal{U}_m|\mu_d|\mathcal{G}_f\rangle}{(\omega_a + \omega_b + \omega_c - \omega_{\mathcal{U}_m})} \right). \tag{10}$$

Analogous to the results for 3PA, we find that the 4PA cross sections are proportional to the TPA cross section, the proportionality factor being the excited-state polarizability divided by an energy term.

For 5-photon absorption, we can in a similar manner write

$$M^{\mathrm{5PA}}_{abcde} = \mathcal{P}^{abcde} \sum_{k,m=1}^{n_{\mathcal{U}}} \sum_{l,n=1}^{n_{\mathcal{G}}} \frac{\langle 0|\mu_a|\mathcal{U}_k\rangle\langle\mathcal{U}_k|\mu_b|\mathcal{G}_l\rangle\langle\mathcal{G}_l|\mu_c|\mathcal{U}_m\rangle\langle\mathcal{U}_m|\mu_d|\mathcal{G}_n\rangle\langle\mathcal{G}_n|\mu_e|\mathcal{U}_f\rangle}{(\omega_a - \omega_{\mathcal{U}_k})(\omega_a + \omega_b - \omega_{\mathcal{G}_l})(\omega_a + \omega_b + \omega_c - \omega_{\mathcal{U}_m})(\omega_a + \omega_b + \omega_c + \omega_d - \omega_{\mathcal{G}_n})}, \tag{11}$$

noting that we now have two *ungerade* intermediate states that can be substituted by the $\mathcal{U}_f$ state. If we only introduce the final state for the second *ungerade* state ($\mathcal{U}_m$ in the equation) we obtain

$$M^{\mathrm{5PA}}_{abcde} \approx \mathcal{P}^{abcde} \left(\frac{M^{\mathrm{3PA}}_{abc}}{(\omega_a + \omega_b + \omega_c - \omega_{\mathcal{U}_f})} \cdot \sum_{n=1}^{n_{\mathcal{G}}} \frac{\langle\mathcal{U}_f|\mu_d|\mathcal{G}_n\rangle\langle\mathcal{G}_n|\mu_e|\mathcal{U}_f\rangle}{(\omega_a + \omega_b + \omega_c + \omega_d - \omega_{\mathcal{G}_n})} \right), \tag{12}$$

which is an expression for *3PA-dominated 5PA* which is representative for the A_u states of the PDNB molecule.[1] In most cases, we can simplify Eq. 12 further by substituting all *ungerade* intermediate states by the final state, giving

$$M^{\mathrm{5PA}}_{abcde} \approx \mathcal{P}^{abcde} \sum_{l,n=1}^{n_\mathcal{G}} \frac{\langle 0|\mu_a|\mathcal{U}_f\rangle\langle\mathcal{U}_f|\mu_b|\mathcal{G}_l\rangle\langle\mathcal{G}_l|\mu_c|\mathcal{U}_f\rangle\langle\mathcal{U}_f|\mu_d|\mathcal{G}_n\rangle\langle\mathcal{G}_n|\mu_e|\mathcal{U}_f\rangle}{(\omega_a - \omega_{\mathcal{U}_f})(\omega_a + \omega_b - \omega_{\mathcal{G}_l})(\omega_a + \omega_b + \omega_c - \omega_{\mathcal{U}_f})(\omega_a + \omega_b + \omega_c + \omega_d - \omega_{\mathcal{G}_n})} \tag{13}$$

$$= \mathcal{P}^{abcde} \left(\frac{M^{\mathrm{OPA}}_a}{(\omega_a - \omega_{\mathcal{U}_f})(\omega_a + \omega_b + \omega_c - \omega_{\mathcal{U}_f})} \cdot \sum_{l=1}^{n_\mathcal{G}} \frac{\langle\mathcal{U}_f|\mu_b|\mathcal{G}_l\rangle\langle\mathcal{G}_l|\mu_c|\mathcal{U}_f\rangle}{(\omega_a + \omega_b - \omega_{\mathcal{G}_l})} \cdot \sum_{n=1}^{n_\mathcal{G}} \frac{\langle\mathcal{U}_f|\mu_d|\mathcal{G}_n\rangle\langle\mathcal{G}_n|\mu_e|\mathcal{U}_f\rangle}{(\omega_a + \omega_b + \omega_c + \omega_d - \omega_{\mathcal{G}_n})} \right),$$

which shows that the 5PA absorption cross section can be expected to be proportional to the OPA transition moment scaled by the excited-state polarizability squared.

These expressions explain why we observe the orthogonality of the odd- and even-order multiphoton absorption cross sections. Furthermore, they also explain the strong parallelity of the odd- and even-order multiphoton absorption cross sections, as they are in all cases related to the lowest-order one- or two-photon absorption cross section, scaled by the energy difference between the excitation energy to the final state and the incoming laser frequencies, and scaled by (products of) excited-state polarizabilities. It is important to point out that this model does not allow quantitative predictions of higher-order MPA from OPA or TPA data but it gives a qualitative to semi-quantitative description of the behaviour of the different properties.

Multiphoton absorption cross sections can be enhanced through resonances, occuring when the frequency (or sums of frequencies) of the incoming laser light matches that of intermediate excited states (*e.g.* when $\omega_a = \omega_{\mathcal{G}_f}/2 \approx \omega_{\mathcal{U}_k}$ in the case of TPA). We note from the equations above that the frequency prefactor in the few-state models has the same poles as that of the TPA or 3PA processes, respectively. Thus, boosting TPA and 3PA

[1] In principle there should also be a term arising from introducing the final state for the first *ungerade* intermediate state. However, this would lead to a term which would correspond to the OPA transition moment scaled by the excited-state second hyperpolarizability, and thus can be expected to be smaller.

processes through near-resonance conditions will also boost the higher-order multiphoton absorption cross section.

Boosting a higher-order multiphoton absorption cross section selectively without a simultaneous increase in the lower-order multiphoton absorption cross section will thus only be possible if we can make the excited-state polarizability approach a pole for one of the frequency combinations of the incoming laser light. Consider for example the 4PA transition moment in Eq. 10. Whereas the TPA cross section, and thus also the 4PA cross section, will have a pole if there are intermediate states at half the energy of the excited state, the 4PA will be selectively enhanced if there is an excited state of *ungerade* symmetry at $3\omega_{\mathcal{G}_f}/4$. Similar considerations can be made for the 5PA process, and we can selectively enhance the 5PA process if there are intermediate states of *gerade* symmetry with energy $2\omega_{\mathcal{U}_f}/5$ and $4\omega_{\mathcal{U}_f}/5$.

If we now return to the unexpected enhancement of the 4PA cross section of the $2B_{1g}$ (and the close-lying $1B_{1g}$ and $1A_g$ states) in PDNB, we note that there exists an intermediate B_{2u} state of *ungerade* symmetry at approximately 3/4 of the energy of these final states, thus creating a resonance in the excited-state polarizability in enhancement of the 4PA process relative to the TPA process.

To summarize our findings, we have presented the first 5PA cross section calculations at the density-functional level of theory using the CAM-B3LYP exchange–correlation functional for three centrosymmetric molecules. These calculations have shown that for molecules with an inversion centre, the selection rules for dipole-allowed transitions make the relative magnitude of all the even (odd) multiphoton absorption cross sections similar for different excited states. Assuming the validity of a few-state model for the states with the same symmetry as the final state of the multiphoton absorption process, we have shown that higher-order multiphoton absorption cross sections are proportional to the TPA (even-order absorption processes) or OPA (odd-order absorption processes) cross sections,

scaled by an energy denominator and powers of the polarizability of the final excited state.

Our analysis shows that for centrosymmetric molecules, excited states that display strong one- or two-photon absorption cross sections will also display strong multiphoton absorption cross sections. We have also shown how to selectively enhance the higher-order multiphoton absorption cross section by designing molecules with intermediate states that match selected frequency combinations for the frequency of the incoming light. We predict, for instance, a strong enhancement of 5PA processes by designing molecules with intermediate states of energy $2\omega_{\mathcal{U}_f}/5$ and $4\omega_{\mathcal{U}_f}/5$, as well as for 4PA as illustrated by our results calculated for the PDNB molecule. These results will be valuable guidelines for designing molecules with strong higher-order multiphoton absorption cross section.

Computational details

All multiphoton absorption calculations have been performed using a recursive open-ended response theory code[19] which has recently been expanded to the treatment of single residues of response functions.[20] This program is a submodule of the Dalton program.[26] All calculations have been performed using the aug-cc-pVDZ basis set from the Dunning family of basis sets[24] and the CAM-B3LYP density functional.[23] In all calculations of n-photon absorption the energy of the involved photons was the excitation energy divided by n.

The geometry of the *para*-dinitrobenzene molecule has been optimized using the cc-pVQZ basis set and the B3LYP-functional[32,33] in Gaussian.[34] The geometries of the di-aminoazobenzene and indigo molecules have been optimized using TURBOMOLE[35] with the B3LYP functional and the TZVP basis set.[36]

The rotational averaging of the calculated results has been performed following available literature[37–39] and the calculation of the cross sections was done using an approach which has recently been generalized by two of us[20] based on work by Peticolas.[27] The detailed

equations for this are given in the supplementary information.

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Some more information about the rotational averaging and of the multiphoton absorption tensors and the conversion from atomic units to cgs unis can be found in the supporting information. This information is available free of charge via the Internet at http://pubs.acs.org/photonics.

References

(1) Göppert-Mayer, M. Über Elementarakte mit zwei Quantensprüngen. *Ann. Phys.* **1931**, *401*, 273–294.

(2) Kaiser, W.; Garrett, C. G. B. Two-Photon Excitation in CaF_2:Eu^{2+}. *Phys. Rev. Lett.* **1961**, *7*, 229–231.

(3) Parthenopoulos, D. A.; Rentzepis, P. M. Three-dimensional optical storage memory. *Science* **1989**, *245*, 843–845.

(4) Zipfel, W. R.; Williams, R. M.; Webb, W. W. Nonlinear magic: multiphoton microscopy in the biosciences. *Nat. Biotechnol.* **2003**, *21*, 1369–1377.

(5) Helmchen, F.; Denk, W. Deep tissue two-photon microscopy. *Nat. Methods* **2005**, *2*, 932–940.

(6) Pawlicki, M.; Collins, H. A.; Denning, R. G.; Anderson, H. L. Two–Photon Absorption and the Design of Two–Photon Dyes. *Angew. Chem. Int. Ed.* **2009**, *48*, 3244–3266.

(7) Zheng, Q.; Zhu, H.; Chen, S.-C.; Tang, C.; Ma, E.; Chen, X. Frequency–upconverted stimulated emission by simultaneous five–photon absorption. *Nat. Phot.* **2013**, *7*, 234–239.

(8) Hettema, H.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J. Quadratic response functions for a multiconfigurational self-consistent field wave function. *J. Chem. Phys.* **1992**, *97*, 1174–1190.

(9) Sałek, P.; Vahtras, O.; Helgaker, T.; Ågren, H. Density-functional theory of linear and nonlinear time-dependent molecular properties. *J. Chem. Phys.* **2002**, *117*, 9630–9645.

(10) Koch, H.; Jørgensen, P. Coupled cluster response functions. *J. Chem. Phys.* **1990**, *93*, 3333–3344.

(11) Paterson, M. J.; Christiansen, O.; Pawłowski, F.; Jørgensen, P.; Hättig, C.; Helgaker, T.; Sałek, P. Benchmarking two-photon absorption with CC3 quadratic response theory, and comparison with density-functional response theory. *J. Chem. Phys.* **2006**, *124*, 054322.

(12) Hättig, C.; Christiansen, O.; Jørgensen, P. Coupled cluster response calculations of two-photon transition probability rate constants for helium, neon and argon. *J. Chem. Phys.* **1998**, *108*, 8355–8359.

(13) Friese, D. H.; Hättig, C.; Ruud, K. Calculation of two-photon absorption strengths with the approximate coupled cluster singles and doubles model CC2 using the resolution-of-identity approximation. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1175–1184.

(14) Jonsson, D.; Norman, P.; Ågren, H. Cubic response functions in the multiconfiguration self-consistent field approximation. *J. Chem. Phys.* **1996**, *105*, 6401–6419.

(15) Cronstrand, P.; Luo, Y.; Norman, P.; Ågren, H. Ab initio calculations of three-photon absorption. *Chem. Phys. Lett.* **2003**, *375*, 233–239.

(16) Cronstrand, P.; Jansik, B.; Jonsson, D.; Luo, Y.; Ågren, H. Density functional response theory calculations of three-photon absorption. *J. Chem. Phys.* **2004**, *121*, 9239–9246.

(17) Zheng, Q.; He, G. S.; Baev, A.; Prasad, P. N. Experimental and Quantum Chemical Studies of Cooperative Enhancement of Three-Photon Absorption, Optical Limiting, and Stabilization Behaviors in Multibranched and Dendritic Structures. *J. Phys. Chem. B* **2006**, *110*, 14604–14610, PMID: 16869561.

(18) Diaz, C.; Vesga, Y.; Echevarria, L.; Stara, I. G.; Starỳ, I.; Anger, E.; Shen, C.; El Sayed Moussa, M.; Vanthuyne, N.; Crassous, J.; Rizzo, A.; Hernández, F. E. Two-photon absorption and two-photon circular dichroism of hexahelicene derivatives: a study of the effect of the nature of intramolecular charge transfer. *RSC Adv.* **2015**, *5*, 17429–17437.

(19) Ringholm, M.; Jonsson, D.; Ruud, K. A general, recursive, and open-ended response code. *J. Comput. Chem.* **2014**, *35*, 622–633.

(20) Friese, D. H.; Beerepoot, M. T. P.; Ringholm, M.; Ruud, K. Open-Ended Recursive Approach for the Calculation of Multiphoton Absorption Matrix Elements. *J. Chem. Theory Comput.* **2015**, *11*, 1129–1144.

(21) Alam, M. M.; Chattopadhyaya, M.; Chakrabarti, S.; Ruud, K. Effect of donor-acceptor orientation on solvent-dependent three-photon activity in through-space charge-transfer systems - case study of [2,2]-paracyclophane derivatives. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17570–17576.

(22) Alam, M. M.; Chattopadhyaya, M.; Chakrabarti, S.; Ruud, K. Chemical Control of Channel Interference in Two-Photon Absorption Processes. *Acc. Chem. Res.* **2014**, *47*, 1604–1612.

(23) Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.

(24) Dunning Jr., T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(25) Woon, D. E.; Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations IV. Calculation of static electrical response properties. *J. Chem. Phys.* **1994**, *100*, 2975–2988.

(26) Aidas, K. et al. The Dalton quantum chemistry program system. *WIREs Comput. Mol. Sci.* **2013**, *4*, 269, doi: 10.1002/wcms.1172.

(27) Peticolas, W. Multiphoton Spetroscopy. *Ann. Rev. Phys. Chem.* **1967**, *18*, 233–260.

(28) Olsen, J.; Jørgensen, P. Linear and nonlinear response functions for an exact state and for an MCSCF state. *J. Chem. Phys.* **1985**, *82*, 3235–3264.

(29) Hättig, C.; Christiansen, O.; Jørgensen, P. Multiphoton transition moments and absorption cross sections in coupled cluster response theory employing variational transition moment functionals. *J. Chem. Phys.* **1998**, *108*, 8331–8354.

(30) Cronstrand, P.; Luo, Y.; Ågren, H. Generalized few-state models for two-photon absorption of conjugated molecules. *Chem. Phys. Lett.* **2002**, *352*, 262 – 269.

(31) Vivas, M. G.; Diaz, C.; Echevarria, L.; Mendonca, C. R.; Hernández, F. E.; De Boni, L. Two-Photon Circular–Linear Dichroism of Perylene in Solution: A Theoretical–Experimental Study. *J. Phys. Chem. B* **2013**, *117*, 2742–2747.

(32) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(33) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(34) Frisch, M. J. et al. Gaussian 09 Revision C.01. Gaussian Inc. Wallingford CT 2009.

(35) TURBOMOLE V6.6 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from
`http://www.turbomole.com`.

(36) Schäfer, A.; Huber, C.; R., A. *J. Chem. Phys.* **1989**, *100*, 5829–5835.

(37) Andrews, D. L.; Thirunamachandran, T. On three-dimensional rotational averages. *J. Chem. Phys.* **1977**, *67*, 5026–5033.

(38) Andrews, D. L.; Ghoul, W. A. Polarization studies in multiphoton absorption spectroscopy. *J. Chem. Phys.* **1981**, *75*, 530–538.

(39) Friese, D. H.; Beerepoot, M. T. P.; Ruud, K. Rotational averaging of multiphoton absorption cross sections. *J. Chem. Phys.* **2014**, *141*, 204103.

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Using a few-state model sketched in the picture we describe the specific five-photon absorption behaviour of centrosymmetric molecules. This gives a deeper insight into the mechanisms of multiphoton absorption.

Keywords

- UV/VIS-Spectroscopy
- Response theory
- Quantum chemistry
- Ab-initio calculations
- Molecular modelling
- Non-linear optical properties
- Structure-activity relations